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Effect of Plasticizers on the Properties of New Ambient
Temperature Solid Polymer Electrolytes

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Abstract - The effect of different plasticizers on the conductivities and physical/chemical properties of radiation-polymerized polyethers formed by cross-linking mixtures of acrylate oligomers and dissolved salts have been studied. The plasticizers used were propylene carbonate, ethylene carbonate and a mixture of ethylene carbonate and propylene carbonate. The conductivities of all the compositions studied were in the range of 10^{-3} to 10^{-4} S/cm. In this paper, the relationship of the conductivities to the physical, chemical, and electrochemical properties of these materials is discussed.

Introduction

Considerable effort has been devoted to synthesizing polymer electrolytes with high room temperature conductivities for use in rechargeable Li batteries and electrochromic windows [1-8]. The goal has been a conductivity of 10^{-3} S/cm or greater at room temperature, and it has seemed very unlikely that it would be achieved with conventional polymer electrolytes such as poly(ethylene oxide) (PEO) and related compounds. Hence most recent investigations have dealt with polymer electrolytes that are mixtures of polymers and plasticizers. One approach [4] has involved encapsulating Li^+ -solvates of organic solvent blends, such as ethylene carbonate/propylene carbonate (EC/PC) and EC/PC/tetraglyme, within a polymer-matrix, such as polyacrylonitrile, which itself contributes relatively little to the ionic conductivity of the resulting electrolyte. Another approach being pursued involves the formation of gel electrolytes containing lithium salts [5-7], materials synthesized either by free-radical polymerization and radiation cross-linking of a macromolecular organic substance such as 2-acrylamido-2-methyl-1-propane sulfonic acid (AMPS) containing LiCF_3SO_3 [7], or by the radiation polymerization of a polyether [5-6] containing LiCLO_4 , LiAsF_6 and LiCF_3SO_3 . The resulting polymer electrolytes have been reported to have conductivities in the range of 10^{-3} S/cm at room temperature.

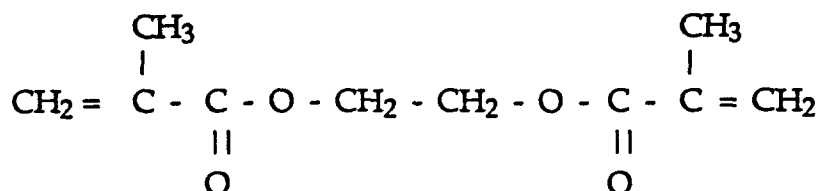
Previous work [5,6] has shown it possible to form a high conductivity polymer electrolyte by the radiation polymerization and cross-linking of a mixture of acrylate oligomers containing plasticizers and dissolved salt. Several new electrolytes prepared in this way have conductivities of 10^{-3} S/cm at room temperature and about 10^{-4} S/cm at 0°C . As would be expected, the plasticizer has a large influence on the physical, chemical and electrochemical properties of the electrolyte. For example, changing the plasticizer from propylene carbonate (PC) to poly(ethylene glycol dimethyl ether) (Poly 500) improved the thermal, mechanical and Li cycling properties of the electrolyte, somewhat at the expense of room temperature conductivity.

This paper reports results of a study of the effect of mixed plasticizers on the conductivities and physical/chemical properties of radiation-polymerized polyether electrolytes. The plasticizers investigated were mixtures of ethylene carbonate and propylene carbonate containing 1M LiAsF_6 . The conductivities of all the compositions studied were in the range of 10^{-3} to 10^{-4} S/cm at room temperature. The mixed plasticizer compositions appear to have better thermal, mechanical and Li cycling properties than those formed with single plasticizers.

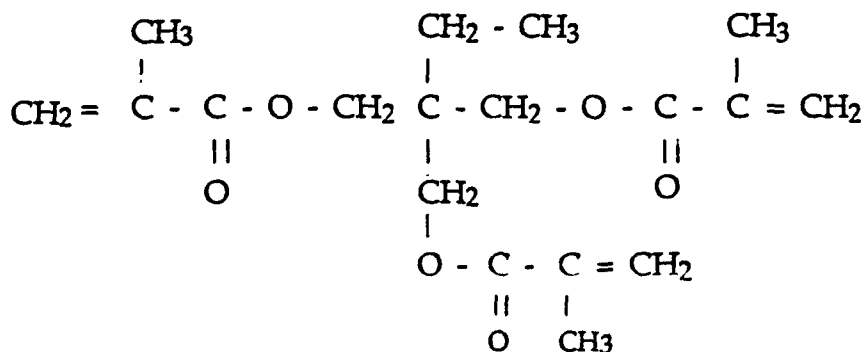
Experimental Procedures

Preparation of Electrolytes: The polymeric electrolyte was prepared by the radiation induced curing of ethylene oxide/acrylate monomers of the type:

ETHYLENE GLYCOL DIMETHACRYLATE



TRIMETHYLOLPROPANE TRIMETHACRYLATE



After curing, the polymer formed a rigid three dimensional structure which lent good mechanical properties to the electrolyte. The high conductivity was realized by plasticizing the polymer with ethylene carbonate (EC) and propylene carbonate (PC) which contained LiAsF_6 salt in a 1 M concentration independent of the plasticizer composition. In addition to the pure plasticizers, EC/PC mixtures in the ratios (weight-%) 25:75, 50:50 and 72:25 were prepared.

Materials Characterization: Physical characterization included differential scanning calorimetry (DSC) and thermogravimetry (TGA). Polymer film conductivities were measured by complex impedance/admittance analysis from 1Hz to 65KHz.

Electrochemical measurements were carried out with a BAS100 electrochemical analyzer (Bioanalytical Systems, Inc.). For electrochemical studies a laminate cell configuration [2] with 9 cm^2 area and electrolyte thickness of $100 \mu\text{m}$ were used. Cells consist of both the symmetrical type, Li/SPE/Li, and the asymmetrical type, Li/SPE/Ni.

Results and Discussion

Differential Scanning Calorimetry: DSC traces for some of the compositions are shown in Fig. 1. The electrolyte with pure EC (Fig. 1A) has two melting peaks: one small peak, T_{m1} , around 26°C and the other, T_{m2} , around 39°C , indicating that the electrolyte is partially crystalline at room temperature. The T_g of this complex is -65°C . When 25% by weight PC is added to the EC (composition 75:25), both peak positions shift to considerably lower values (Fig. 1B), 8°C and 15°C , respectively. Not only the melting peaks shift to lower values, T_g also shifts to a lower value of about -75°C . Although the electrolyte is now amorphous at room temperature, it is still partially crystalline at lower temperatures. When 50% PC is added to EC (50:50, Fig. 1C), both the melting peaks T_{m1} and T_{m2} disappear completely rendering the electrolyte completely amorphous from about -90°C to 150°C and shifting the T_g to an even lower value of about -94°C . Further increase of the PC/EC ratio does not change the DSC results. In fact, the DSC traces of electrolytes having PC contents of 50:50 and higher are very similar to the DSC of pure PC [6].

Thermogravimetric Analysis: A typical TGA scan for an electrolyte composition containing mixed EC/PC as the plasticizer is shown in Fig. 2. The particular composition in this case is EC/PC, 75:25. As can be seen from the figure, the decomposition of the electrolyte occurs in two steps. The maximum weight loss for the two processes are about 198°C and 230°C respectively. The weight loss at 100°C and 150°C and the peak derivative temperature for all the compositions of the electrolytes studied are summarized in Table 1. It is evident from the Table that composition 50:50 is thermally the most stable, with weight loss of only 0.36% at 100°C ; whereas pure PC is the least stable with 3.28% weight loss at the same temperature. The thermal stability of 50:50 composition is comparable to

Poly 500 [6]. The decomposition of electrolytes containing pure EC and mixed plasticizers takes place in two steps, whereas that of pure PC occurs in a single step.

Physically and mechanically the mixed compositions are completely transparent and rubbery, whereas those formed with pure EC or PC tend to be slightly milky and brittle.

Conductivity Results: The room temperature conductivities of the different electrolyte compositions are summarized in Table 2; the value for an electrolyte containing Poly 500 as the plasticizer is included for easy reference [6]. The electrolyte composition containing pure PC has the highest room temperature conductivity, about 2.3×10^{-3} S/cm, and that with pure EC is lowest, about 5×10^{-4} S/cm, as would be expected since it is partially crystalline at room temperature. The conductivities of the mixed compositions fall between these two extremes. The conductivities of electrolytes with 50:50 and higher PC contents are only marginally lower ($\sigma > 8.0 \times 10^{-4}$ S/cm) than that of pure PC. As mentioned previously, electrolytes formed with pure PC are not thermally stable above room temperature [6] and have poor dimensional stability. By incorporating EC into the plasticizer mixture, it has been possible to maintain the desirable properties of PC, such as low T_g and a completely amorphous structure, while greatly improving the thermal and mechanical properties without a large compromise in conductivity.

Electrochemical Properties: Cyclic voltammetric studies on symmetrical Li/SPE/Li cells show that the electrolytes with plasticizer compositions from 50:50 to pure PC are stable at least up to +3.5V vs. Li/Li⁺ [8]. The plating-stripping process of lithium from these electrolyte compositions was investigated on a nickel substrate. When the Ni electrode in an asymmetric cell of the type, Li/SPE/Ni, is swept cathodically (1-5mV/sec) for an electrolyte containing just EC, an irreversible reduction peak occurs around 1.3V, which diminishes with cycling but does not disappear, followed by the plating of Li onto the Ni electrode beginning around -0.18V. Upon reversing the scan, the stripping of Li is observed, with the current peaking around 0.28V; no other oxidation peak is observed up to +2.4V vs. Li/Li⁺. For electrolytes with mixed plasticizer compositions from 50:50 to higher PC content, the irreversible peak around 1.3V is completely absent and lithium plating and stripping peaks occur between -0.4 and +0.4V vs. Li/Li⁺. No other peaks appear up to 3.2V vs. Li/Li⁺. Lithium plating and stripping in these cases appears quite reversible and does not change appreciably with extended cycling after the first cycle. These preliminary results indicate that the polymer electrolytes containing mixed plasticizers are electrochemically quite stable.

Conclusions

Among polymer electrolyte compositions formed by incorporating mixtures of PC and EC and dissolved salts into a polymer network of radiation-polymerized polyethers formed by cross-linking mixtures of acrylate oligomers, compositions containing a 50:50

PC/EC mixture are the most stable while those formed with pure PC are the least stable. The use of EC along with PC succeeds in maintaining the desirable properties of PC, such as a low T_g and a completely amorphous structure, while avoiding the low thermal stability encountered with pure PC.

The conductivities of electrolytes containing 50:50 and higher PC content are only slightly lower ($\sigma > 8 \times 10^{-4}$ S/cm) than that containing pure PC ($\sigma = 2.3 \times 10^{-3}$ S/cm), which has the highest conductivity of all the compositions studied. However cells formed with electrolytes containing pure PC appear to be more prone to lithium dendrite formation than those formed with mixed electrolyte compositions. Preliminary studies on the mixed plasticizer compositions indicate that lithium plating and stripping on a Ni electrode are reproducible and reversible, at least during cyclic voltammetry experiments.

Acknowledgements

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Figure Captions

Figure 1. DSC traces of the polymer electrolytes with 1M LiAsF₆ and EC:PC composition of (1) 100:0, (2) 75:25, (3) 50:50, at 10°C/min.

Figure 2. TGA trace of 1M LiAsF₆ with EC:PC composition of 75:25 at 10°C/min.

Table 1

**TGA Results
1M LiAsF₆**

Plasticizer Composition EC:PC	Wt. loss at 100°C	Wt. loss at 150°C	Peak Temp ₁ °C dwt/dT	Peak Temp ₂ °C dwt/dt
100:0	1.78	8.03	202°	237°
75:25	1.84	12.14	198	230
50:50	0.36	6.86	214	238
25:75	2.30	11.07	203	216
0:100	3.28	21.06	160	---
*Poly 500	0.2	0.7	238	---

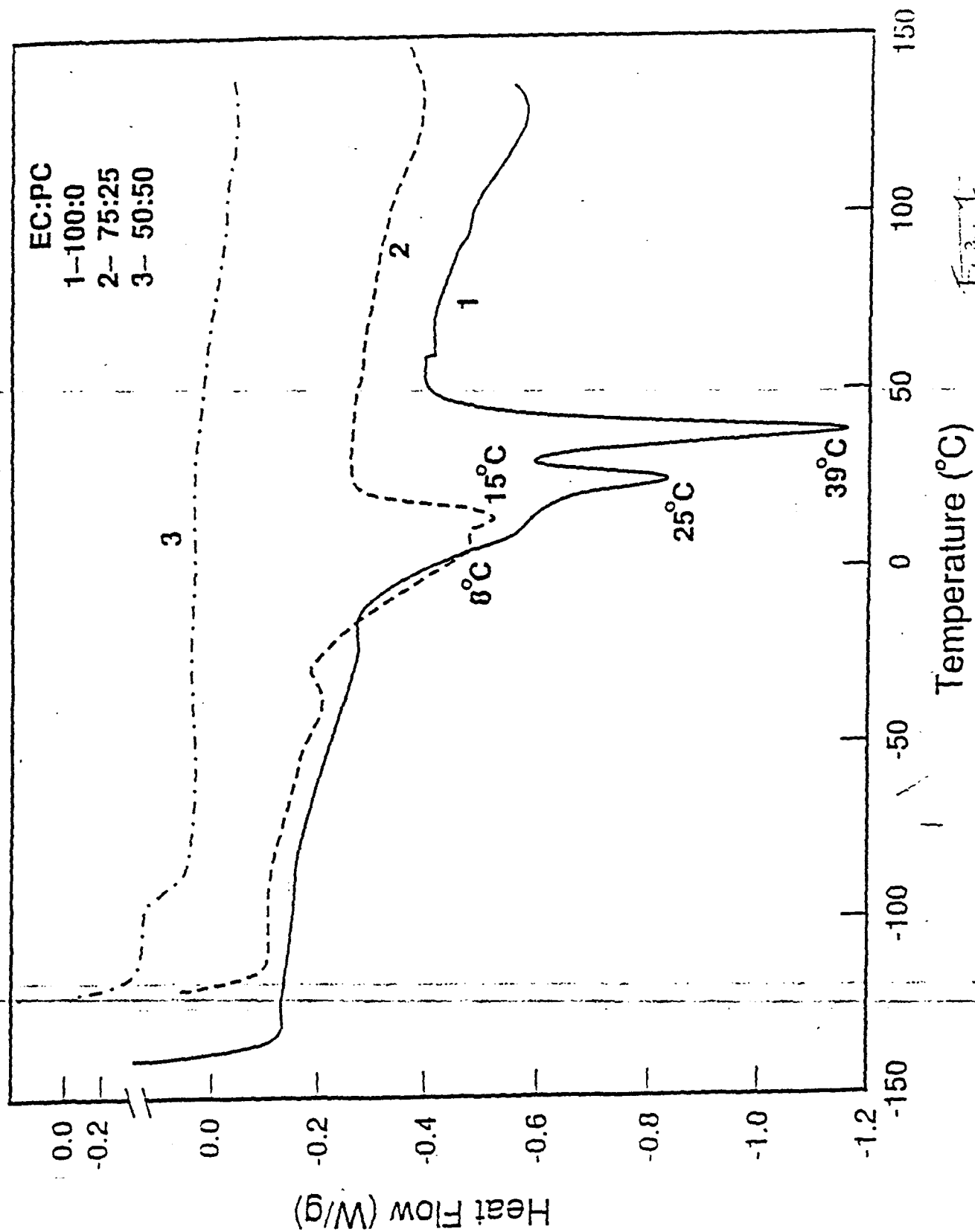
Table 2

**Room Temperature Conductivity Results
1M LiAsF₆**

Plasticizer Composition EC:PC	Conductivity S/cm
100:0	5.0×10^{-4}
75:25	7.35×10^{-4}
50:50	8.43×10^{-4}
25:75	9.77×10^{-4}
0:100	2.25×10^{-3}
*Poly 500	1.95×10^{-4}

*Ref. 8

DSC



TGA

